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NATIONAL BUREAU OF STANDARDS REPORT

9833

HEALTH DANGERS DURING THE MANUFACTURE PROCESSING AND DECOMPOSITION OF SYNTHETIC PRODUCTS

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TRANSLATION

by

Mrs. M. Vaishnav

of

Selected Portions of Article Published
in
''Moderne Unfallverhutung'' (Modern Accident Prevention),
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NBS

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

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Decomposition and Incomplete Combustion Products of Synthetics (p 23)

We shall discuss shortly those products that can appear from the thermal decomposition, specifically combustion, of synthetics. Basically, we can say that only in exceptional cases will the building blocks of the synthetic again be liberated. The fear of such decomposition products likely came about because those working with Teflon decomposition appeared to get fever attacks. As with the inhalation of zinc oxide fog, there suddenly appear in healthy people, after the inhalation of decomposition products of Teflon, short fever attacks which are without consequence. The next day people are again completely healthy [90]. The cause for these fever attacks is not the monomer ($CF_2 = CF_2$), a slightly narcotic gas, which is deadly for rats only in a concentration of 4 percent after 4 hours inhalation [63]. Teflon is amazingly heat stable. Only above 300 °C, that is in the vicinity of the melting point of lead (327 °C), Teflon begins to decompose, in the process of which a fine sublimate appears, on which hydrogen fluoride could possibly adsorb. Hydrogen fluoride causes lung damage with inhalation of long duration, but no fever attacks which disappear after a short time. At temperatures above 400 °C, Teflon produces toxic decomposition products of oligomer structure such as C_4F_8, which can appear as Perfluorisobutylen or Perfluorcyclobuten. However, these materials can not be the cause of the Teflon fever either, since they do not cause a temperature rise [91].

Interestingly enough, Teflon fever has been observed in America after smoking of cigarettes which had been contaminated with Teflon dust. Surely, Teflon does not belong in cigarettes or tobacco. The claim, however, that a surgeon who used a Teflon fabric as an artificial blood vessel and died after smoking a Teflon contaminated cigarette after completing the operation, is completely grabbed out of the air, even though this claim continues to appear in various newspapers [63, 92]. The decomposition products of the half-synthetic man-made material, nitrocellulose, have, however, cost many people's lives decades ago. In the year 1929 a fire broke out in a clinic in Cleveland, Ohio, which spread to the X-ray film storage room. In those days, X-ray films were made of nitro-cellulose. Nitro-cellulose burns so well that with the addition of oxygen, neither nitrous gases nor carbon monoxide can appear. In Cleveland, through a chain of unfortunate circumstances, great masses of carbon monoxide and nitrous gases were formed from the nitro-cellulose film, spreading throughout the lab and killing 125 people [93].

Possibly, because of this Cleveland catastrophe, all combustion products of man-made materials are feared by fire-knowledgeable people. At any rate, the Plastics Standards Board formed a special Lower Board which concerns itself with the question of the chemistry and toxicity of the incomplete-combustion products of man-made materials. In our Institute, we have for many years worked experimentally on this question. In modification of an idea by Scholz (Hoechst), an apparatus, similar to the combustion oven used by the chemist for the study of combustion products, was made in our Institute by Kett and Poeschl many years ago.

The combustible materials are spread evenly on a boat, 30 cm long, 2 cm wide made of glass or quartz. The boat is put in a "combustion tube" made of glass or quartz (25 millimeter diameter, 120 cm long). Above this is placed a regulatable cylindrical heating oven. Through the combustion tube - in a counter flow to the heat from the oven - 100 liters of air per hour flow over the heated glass "boat" with the combustible products. The airstream with the volatile combustion products is mixed at the other side of the oven with 100 liters per hour of fresh air, through which the combustion vapors are cooled and supplied with enough oxygen. This mixture streams through a distributor through 6 small inhalation chambers, each of which contains a rat. The exposure time of the rats is generally 30 minutes. The combustion, in each experiment, takes place at constant temperature. Generally, all materials are repeatedly tested at 300, 400, 500, and 600 degrees Centigrade.

As is well known, complete combustion of natural organic materials (without nitrogen) results in CO_2 and H_2O, while incomplete combustion results in CO. If the natural materials contain Nitrogen, you may get NH_3, amino acids, HCN. With Hofmann & Meineck (BASF), we examined not only artificial materials, but high molecular weight natural materials such as wood, cork, rubber, felt or leather. To compare exactly the danger of the incomplete combustion products from the natural and artificial materials, we always started with equal weight (5 g) samples. Aside from

other combustion products, we always approximately checked the CO concentration shortly in front of the inhalation chamber by sampling with Draeger tubes, and at end of each test, quantitatively checked the CO-Hb concentration in the blood of the rats (Fretwurst-Meinecke Method) [94].

The rats exposed to the incomplete-combustion products that form from natural and man-made materials between 300 and 600 °C succumbed, nearly without exception, to CO poisoning. Table 17 shows the CO concentration in the inhalation air and, which is more important, in the blood of the rats at the conclusion of the experiment; it also shows the number of animals that died. This table shows that the incomplete-combustion products of most of the man-made materials are much less toxic than those of natural materials. One exception is PVC which through its high chlorine content gives off HCl during incomplete combustion which severely aggravates the mucous membranes in the inhalation passages.

For particular reasons, various foam polystyrenes, which play a large role as insulation material in building, were examined in depth. This material also is much less dangerous than the comparison tested insulation material of expanded cork.

As shown in Table 18, at considerably differing temperatures, the various materials begin to smolder forming large quantities of CO which may have a deadly effect. Felt does not smolder, even at higher temperatures. Here the animals did not die of CO poisoning, but from other incomplete-combustion products, including probably HCN.

That the incomplete-combustion products of wool, silk and other nitrogen-containing natural materials can also contain HCN was shown in the U. S. [63,95]. (Figure 38). Other studies show that CN-rich Polyacrylonitrile, i.e. Dralon or Orlon produces hardly any acrylonitrile under thermal decomposition, and with burning produces CO_2, H_2O and NO_2. Only in very exceptional cases, such as very little oxygen concentration, is HCN obtained from polyacrylonitrile. The fear of these combustion products even here is not justified since in general there is so much oxygen present, that no dangerous quantities of HCN are produced. Care is required in translating animal experiments to humans, as a small example in reference to thermal decomposition will show. In view of the claim that heated propylene glycol produces dangerous decomposition products, for 8 hours we passed air over heated propylene glycol and then into the chambers of rats, similar to the incomplete-combustion products experiments. (Table 19). No rats died when the propylene glycol was heated to 100 or 110 °C. We were, however, very much surprised as we examined the harmless natural materials, peanut oil and olive oil for comparison. Already after four hours of exposure to the thermal decomposition products of olive or peanut oil, heated to 110 °C, practically all the rats died!

It can not be a question of Acrolein because glycerin, at the same temperature and an 8-hour exposure time, did not cause any deaths among the rats. Were the deaths possibly caused by the unsaturated fatty acids that are produced from the oil at 110 °C? We know, how often olive or peanut oil is heated to more than 110 °C in domestic or commercial kitchens. We also know that sometimes mucous membrane irritating decomposition products are formed. However, in contrast to our rats, no one has yet died from them. Thus, the thermal decomposition products of olive and peanut oil are plainly not as dangerous indeed as the animal experiments would indicate - much less still those of propylene glycol or man-made materials.

It is important with all animal experiments, especially in the examination of new materials, to also test natural materials or at least chemical products, whose effect on man has been known for decades or centuries. This has been repeatedly emphasized in the above. The advantages of the animal experiments in the testing of new products are the clear experimental conditions. The difficulty is always the specific reaction of the various types of animals and the inference on man. Equally important as animal experiments in the determination of possible health dangers through working materials is the supervision of the plant in which the materials are manufactured by critical doctors and critical safety engineers. Only in close working cooperation between safety engineers, industrial physicians and manufacture toxicologists is it possible to recognize health endangering working materials in time and to ban health dangers from the working place. This applies not only for the manufactur of man-made materials.

CONCLUSIONS

1. Synthetics are formed — mostly catalytically spead-up — by the assemblage of many building blocks (= Monomer) into macromolecules. Self-polymers are formed from the same kind of building blocks, while co-polymers are formed from differing building blocks.

2. The macromolecules, and therefore the completely polymerized synthetics, are completely non-toxic. They are not reabsorbed by the skin and mucous membranes and they are not attacked by the body acids.

3. The complete nonirritance of the synthetics was best proven by their implantation into the animal and human organism. Since they heal-in without any infectious reaction, they have become essential materials in surgical techniques.

4. There is neither a "Synthetics Cancer" nor a "Polymer Cancer". In rats, there appears sarcoma only after the implantation of large-surfaced foreign objects, such as foils of various chemical nature (noble metal, ivory, silk, man-made materials), but not after the implantation of these materials in the form of threads or powder.

5. Synthetics are not sensitizing. Contingent skin infection through synthetic textile fabrics can be caused by accompanying substances, coatings, dressings, dyestuffs, etc. in faulty manufacture.

6. In the preparation and manufacture of phenol plastics and amino plastics (e.g. glue), sensitizing of the skin and irritation of the mucous membranes can occur from formaldehyde derivatives. Formaldehyde can also be released in the improper manufacture of chip and press boards, which can lead to irritation but not poisoning.

7. The most important synthetics monomers, such as ethylene, propylene, ε-caprolactan, dicarboxylic acid, vinyl chloride, etc., are non-toxic and nonirritating. With toxic or skin-irritating monomers, to which belong the acryl-acid-derivatives (e.g. methyl acrylate, acrylonitrile, acrylamide), the MAC value should not be exceeded at the working place.

8. Among the plasticizers, which are used only for Polyvinylchloride, orthocresol-containing cresylphosphate has caused nerve damage, when it accidentally got into food. The most important plasticizers, the phthalic acid esters, are completely non-toxic. The phthalic acid anhydrid needed for their manufacture only acts as a sensitizer and skin irritant in impure form through maleic acid anhydride or naphthoquinone.

9. Among the synthetics solvents, contrary to misleading data, styrene causes only mucous membrane irritation, not blood damage as does benzol; tetrahydrofurane causes only skin irritation, no liver and kidney damage; dimethylformamid causes essentially less liver damage than carbon tetrachloride; methylglycol, however, causes damage to the mental functions in man, and leucopenia in animal experiments.

10. Among the catalysts, especially dangerous are several organic peroxides, that even in the form of steam can cause skin- and strongest mucous membrane degeneration (blindness). Some tin stabilizers act similar. Hydroquinone causes local depigmentation and in animal experiments it has caused blood damage.

11. Careless manufacture of epoxy resins and lacquers can cause skin damage and exzema through several organic amino hardeners. This is surely avoidable if appropriate care is taken.

12. The processing of the volatile diisocyanate for the manufacture of Polyurethane lacquers must be carried out with very good ventilation (MAC - value of Toluene diisocyanate is 0.02 ppm) in order to avoid damage and sensitizing of the breathing passages. The new isocyanate-lacquer bases have such low volatility that they can be processed without danger.

13. The thermal decomposition and incomplete combustion products of man-made materials are less toxic than the incomplete combustion products of natural materials such as wood, cork, wool or silk, which, under identical experimental conditions, produced more carbon monoxide. An exception is teflon, whose decomposition products can lead to short fever attacks, and polyvinyl-chloride whose decomposition products can lead to mucous membrane irritation.

14. Completely polymerized, clean synthetics have so little effect biologically that they can be used in implants in surgery and in food packaging without health danger. Their processing poses no health dangers. Of the building blocks used in their manufacture, few are toxic or skin irritating. Even those that are can be processed without health danger if a little care is exercised.

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TABLE 17

Acute Inhalation Toxicity of Incomplete-Combustion Products of Various Materials

Temperature - 300 ^{o}C, Exposure Time - 30 min.
Number of Rats/Material - 12

Material (5g)	CO in the Smoke (ppm)	CO-Hemoglobin %	Deaths
Leather	4000	67	+12
Felt	1200	23	+ 6
Wood	1000	32	+ 3
Sheep Wool	500	<15	+ 2
Rubber	25	<15	0
Polyethylene	200	<15	0
Polypropylene	200	<15	0
Polystyrol	25	<15	0
Polystyrene Foam P	25	<15	0
Polystyrene Foam F	20	<15	0
Polyvinyl Chloride	10	<15	+10

Acute inhalation-toxicity of the incomplete-combustion products of natural and man-made materials for rats with equal-quantity initial products and a smoldering temperature of 300 ^{o}C. Dangerous is above all the CO that is produced. Concentrations of under 15% CO-Hemoglobin could not be determined with the method used (Fretwurst-Meinecke). They are, however, toxicologically uninteresting. Only with Polyvinylchloride was the death of the animals not due to CO poisoning, but to a severe inflammation of the respiratory passages due to the hydrochloric acid produced during the decomposition of PVC (Experiments with Hoffman and Meinecke BASF).

TABLE 18

Inhalation of the Incomplete-Combustion Products
Of Natural and Man-Made Materials

Exposure Time: 30 min.
Number of Rats: 12 each

Incomplete Combustion at	300 °C		400 °C		500 °C		600 °C	
Material (each 5g)	CO-Hb	Deaths	CO-Hb	Deaths	CO-Hb	Deaths	CO-Hb	Deaths
Polystyrene Foam P	<15%	0	<15%	0	<15%	0	80%	11
Polystyrene Foam F	<15%	0	<15%	0	19% 75%	0 12	81%	12
Expanded Insulation Cork	17%	0	59%	1	86%	12	87%	12
Rubber	<15%	0	78%	12	75%	12	72%	12
Sheep Wool	<15%	2	19%	12	27%	12	31%	12
Pine Wood	32%	3	86%	12	85%	12	85%	12
Felt	23%	6	27%	12	28%	12	38%	12
Leather	67%	12	69%	12	63%	12	54%	12

Comparison of the toxicity of incomplete-combustion products between 300 °C and 600 °C of natural and man-made materials. The shaded areas indicate the temperature at which the material began to smolder, thereby producing especially large quantities of carbon monoxide. The death of the rats was due nearly without exception to carbon monoxide poisoning. Organic protein-containing materials such as Sheep Wool or Felt also act deadly through other incomplete-combustion products, among them hydrocyanic acid (Experiments with Hoffmann and Meinecke BASF).

TABLE 19

Material	Temp °C	Inhalation Time (Hours)	Number of Deaths per Number of Rats
Olive Oil	100	8	0/6
	110	4	+12/12
		2	0/6
Peanut Oil	110	4	+ 5/6
Glycerin	110	8	0/6
Propylenglycol	110	8	0/6

Toxicity of decomposition products produced by heated olive oil, peanut oil, glycerin and propyleneglycol. The most toxic are the thermal decomposition products from olive oil and peanut oil (Experiments with H. Th. Hofmann).

FIGURE 38

$H_2C = CH - CN$

Acrylonitrile

$$H_2C = \underset{CN}{\underset{|}{CH}}$$

polymerizes to

$$\left[-CH_2 - \underset{CN}{\underset{|}{CH}} - CH_2 - \underset{CN}{\underset{|}{CH}} \;.\;.\;.\;.\;.\; CH_2 - \underset{CN}{\underset{|}{CH}} - \right]_n$$

Polyacrylonitrile: Dralon-, Orlon-fibers

Combustion Products $CO_2 + H_2O + NO_2$

Incomplete-combustion Products $CO_2 + CO + NO + NH_3 + HCN$ little

similarly wool, silk, etc.

The incomplete-combustion products of the CN-rich polyacrylonitrile Dralon and Orlon correspond to the incomplete-combustion products of wool and silk, Only under unfavorable circumstances do nitrogen-containing natural and man-made materials produce hydrocyanic acid.

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